LETTER

Reply to Catalán: Double-proton-transfer dynamics of photo-excited 7-azaindole dimers

The letter by Catalán (1) is concerned with the nature of double-proton transfer in dimers of 7-azaindole (7-AI), and the pertinent issue is whether or not the reaction is concerted. The subject is not new, and, for organic reactions, it has been discussed in the literature for decades. It is now understood that the concerted/consecutive mechanism has to be defined based on the timescale of the vibration motions and the family of coherent trajectories involved (ref. 2 and references therein). For double-proton transfer in isolated dimers, this timescale criterion has been invoked, and, as supported by a variety of time-resolved experiments in several groups and also by theory (ref. 3 and references therein), the conclusion is that the reaction is not concerted on the timescale of the vibrations involved; Catalán and some researchers (see ref. 3) assert that the two protons move in exact concert, maintaining the C_{2h} symmetry at all times.

In the solution phase, we have studied effects of medium polarity and deuterium isotope substitution on the dynamics, and we concluded that the transfer is not concerted (3). Recently, Hsieh *et al*. (4), using a novel series of related structures, also reported evidence of the nonconcerted behavior. Catalán (1) strongly asserts that, using low-resolution conventional absorption/emission measurements, the reaction is concerted (see refs. 1 and 3). He further argues that ground-state H-bonded dimers of 7-AI in polar solvents are not formed. At room temperature and especially in polar solvents the spectra are broad, and neither he nor we can isolate a separate dimer band. In fact, authors of ref. 4 have noted that Catalán's way of analysis is not conclusive. In solution, what is significant is the time resolution together with the effects on the rates of concentration, polarity, and isotope substitution.

In polar solvents, Catalán (1) claims that his excitation spectra are conclusive evidence for the absence of dimers. However, first, as we stated in ref. 3, in acetonitrile the systematic and relatively smaller (than in nonpolar solvents) change at the dimer wavelength was enough to extract a dimer formation constant, as shown in the linear relationship in the lower panel of figure 2, a trend also found for diethyl ether and dichloromethane. We explicitly noted in the text and supporting information that we used the Beer–Lambert formulation for the case of overlapping spectra (3). Second, for highly concentrated solutions, the interpretation of excitation spectra is in doubt; in fact Catalán was criticized in a commentary by Chou *et al.* (5) on distortions in his excitation spectra. Third, Catalán does not address our observed trends, which give K_{eq}, nor does he consider the observed significant change of rates with polarity and isotopic composition made for a series of proton inventory experiments, all reported in ref. 3.

To address the presence of 7-AI dimers and their dynamics, one should not only carefully perform steady-state spectroscopic measurements, as Catalán did, but also examine the time-resolved behavior at different wavelengths (3). Emission spectra of concentrated 7-AI in acetonitrile (figure 2 in ref. 3) clearly display the buildup of a band around 500 nm, which is widely accepted as a signature of excited-state double-proton transfer in 7-AI dimers; similarly, the data of concentrated 7-AI in diethyl ether and dichloromethane show appreciable emission around 500 nm. We feel that Catalán's claim, which is solely based on low-resolution steady-state measurements and "fixed-geometry" electronic structure calculations, cannot reflect the nature of the dynamics, either in the isolated molecule or in solution.

Perhaps the most critical issue is the meaning of concertedness. In a number of papers published on the subject, Catalán did not clearly define the timescale of concertedness, nor did he show how he asserted concertedness from time-averaged low-resolution data, putting aside previous findings from time-resolved experiments and high-quality theory, which are at odd with his claims (see refs. 1 and 3). As pointed out in our recent publication (3), another group of researchers stated, "The concerted mechanism, by its definition, does not require such a strict simultaneity, but it only means that the motions of the two protons are correlated" (6). It seems to us that the initial strict definition of concertedness (with the C_{2h} symmetry path) is now softened toward a breakage of C_{2h} symmetry and asynchronous motions.

At the end, it seems not profitable to have in the scientific literature the same claims in different colors, and we hope that this letter will be the epilogue.

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The authors declare no conflict of interest.

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